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THE STRUCTURE OF ISOLACTARORUFIN

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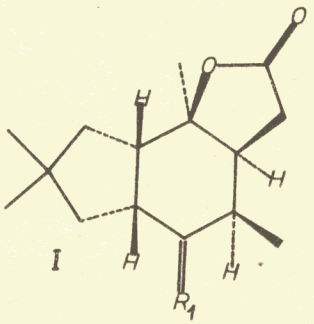
Isolactarorufin (syn. lactarorufin C), a metabolite of Lactarius rufus, is one of the sesquiterpenes isolated from the milky juice of that mushroom[1]. The structure of the carbon skeleton of isolactarorufin was determined on the basis of NMR spectra of 2,3-anhydroisolactarorufin[2]. As a result of the chemical transformation of isolactarorufin into its anhydroderivative two asymmetric centres were missing. Their relative configuration was suggested[2] on the analogy to the configuration of corresponding centres in the lactarorufin B derivative (III, R_3=p-Br-C_6H_4CO-)[3,4].

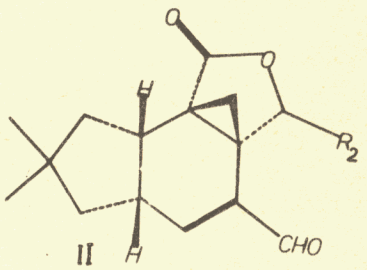
We have performed an X-ray analysis of the crystal structure of isolactarorufin p-bromobenzoate (IV). Crystals were grown from ethyl ether. Preliminary investigations were carried out on a precession camera.

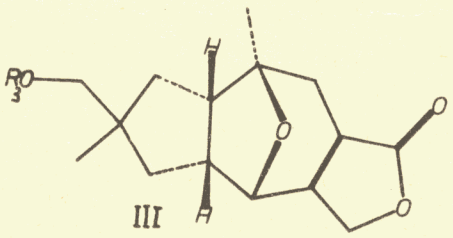
Crystal data:

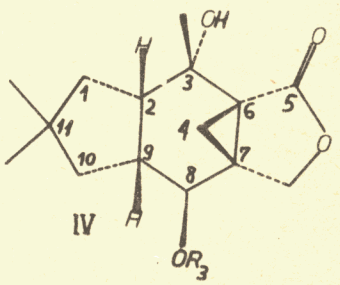
$C_{22}H_{25}O_5Br$, MW=449, m.p. 208.5-210°C, trigonal, space group $P3_1$ or $P3_2$, a=b= 15.58(2), c= 7.73(1), V= 1534 Å^3, D_m= 1.47, D_x= 1.46 g×cm^{-3} Z= 3, F(000)= 696.

Intensities were measured on a Syntex $P2_1$ diffractometer.









The structure (IV, R_3= p-Br-C_6H_4CO-) was solved by the heavy-atom method. Final R-factor = 5.1% for 1176 reflections. Standard deviations of the bond lengths are less than 0.02 Å, valency angles are less than 1.5°. The mean sp^3-sp^3 bond length is 1.546 Å; the aromatic sp^2-sp^2 is 1.385 Å.

The relative configuration of (IV) at C(2) and C(9) is identical with that of the corresponding centres in the terpene illudol (I, R_1= p-Br-C_6H_4NHN=) and marasmic acid (II, R_2= Cl-) derivatives[5]. On the basis of the known absolute configuration of C(2) and C(9) in (I) and (II) and the common biogenesis of illudoids, we propose the absolute configuration for (IV). The configuration of (IV) at C(3) is reverse to that suggested earlier[2].

The intermolecular hydrogen bond between lactone carbonyl oxygen at C(5) and hydroxyl oxygen at C(3) in crystal of (IV) forms a helicoidal system around $P3_1$ axis.

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